NASA Contractor Report 2942



Definition of Air Quality
Measurements for Monitoring
Space Shuttle Launches

Roger D. Thorpe

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TABLE OF CONTENTS

		rage
	SUM	MARY
I.	INI	PRODUCTION
II.	DES	SCRIPTION OF GROUND CLOUD
	Α.	Composition
	В.	Properties at Stabilization 6
	c.	Cloud Motion
		1. Upper Cloud
		2. Lower Cloud
		3. Weather Patterns
III.	AME	SIENT AIR QUALITY AND MONITORING PROGRAMS IN EAST CENTRAL
,		PRIDA
	Α.	Sources of Pollutants
	В.	Air Quality Standards
	c.	Florida State Monitoring System 12
IV.	SPA	CE SHUTTLE LAUNCH SCHEDULE
٧.	MEA	SUREMENT REQUIREMENTS
	Α.	Overview of Air Quality Monitoring
		1. General Considerations
		2. Specific Considerations for Space Shuttle 15
	В.	Monitoring Requirements for KSC
	С.	Monitoring Goals
		1. Short Term
		2. Long Term
		3. Airborne Sampling
	D.	Monitor Siting
		1. HCl Detectors
		2. Acid Rain Monitors
		3. $\mathrm{NO}_{\mathbf{x}}$ and Particulate Monitors
	Ε.	Summary of Measurement Requirements

														Page
VI.	CANDIDATE INST	FRUMENT SYSTEMS	s							•				. 24
	A. HCl Monito	oring Methods .								•				. 24
	1. X-Ray	Fluorescence/Fi	ilter Met	hod		•		•	•	•		•		. 25
		ed Luminol Cher	\cdots	cenc	e/Sa •••	mp]	ling	3 .	•	•		•		. 25
	3. Microco	oulometer/Sampl	ling Tube	Met	hod.			•	•	•				. 26
	4. Compari	ison and Summat	tion						•					. 26
•	B. NO _x Monito	oring Methods .				•			•					. 27
	1. Manual	Techniques							•					. 27
	2. Automat	tic Monitors				•		•	•					. 27
	3. Compari	ison and Summat	ion						•					. 28
	C. Particulat	e Monitoring M	Methods .			•								. 28
	1. Manual	Techniques				•		•	•	•				. 29
	2. Automat	ic Methods				•		•	•				•	. 30
	3. In Situ	ı and Remote Mo	nitoring								•			. 30
	4. Compari	ison and Summat	ion			•		•					•	. 31
	D. Acid Rain	Monitors				•		•	•	•	•	•	•	. 31
VII.		EASUREMENT SYST												
	A. Short Term	n Assessment:	HC1 Moni	tori	ng .	•		•	•	•	•	•	•	. 32
	1. Instrum	ent Selection.		• •		•		•	•	•	•	•	•	. 32
	2. Instrum	ent Siting				•		•	•	•	•	•	•	. 33
	B. Long Term	Assessment: N	$10_{ m X}$ and P	artio	cula	te	Mon	iit	or	ing	3.	•	•	. 33
	1. Instrum	ent Selection.				•		•	•	•	•	•	•	. 33
	2. Instrum	ent Siting				•		•	•	•	•	•	•	. 35
	C. Acid Rain M	fonitoring				•		•	•	•	•	•	•	. 35
	D. Airborne Sa	ampling				•		•	•	•	•	•	•	. 35
	E. System Cost	s				•		•	•	•		•	•	. 35
77 T T T	DEFEDENCES							_	_					- 27

LIST OF TABLES

<u>Table</u>		<u>P</u>	age
I	SHUTTLE EXHAUST PRODUCTS		39
II	APPROXIMATE GROUND CLOUD COMPOSITION AT STABILIZATION		40
III	WIND DIRECTION PROBABILITIES FOR CENTRAL FLORIDA		41
IV	1975 EMISSION ESTIMATES FOR BREVARD COUNTY		42
v	1976 EMISSION ESTIMATES FOR LOCAL POWER PLANTS		42
VI	SECONDARY NATIONAL AIR QUALITY STANDARDS FOR PARTICULATES, NO2, AND SO2		43
VII	ALLOWABLE LIMITS FOR HC1		43
VIII	INDIVIDUAL SAMPLE RESULTS FROM TI-CO AIRPORT FOR THE PERIOD 20 NOVEMBER 1976 TO 7 JANUARY 1977		44
IX	COMPARISON OF SHUTTLE AND LOCAL POWER PLANT EMISSIONS	, •	45
X	HC1 MONITORING TECHNIQUES		46
XI	AMBIENT NO $_{\mathbf{x}}$ MONITORING TECHNIQUES		47
XII	PARTICULATE MONITORING TECHNIQUES		47
XIII	ESTIMATED COSTS OF A REPRESENTATIVE AIR QUALITY MONITORING SYSTEM	, •	48
Figure	LIST OF FIGURES		
1	CLOUD VOLUME AND VELOCITY FOR TITAN III GROUND CLOUD PRIOR TO STABILIZATION (MAY 20, 1975 LAUNCH)	, .	51
2	CLOUD STABILIZATION MEASUREMENTS, DECEMBER 1973 TO SEPTEMBER 1975		52
3	MAXIMUM DOWNWIND HC1 CONCENTRATION		
4	MAXIMUM DOWNWIND HC1 DOSAGE		54
5	LOCATIONS OF AMBIENT AIR QUALITY MONITORING SITES IN KSC AREA		
6	FLORIDA DER SAMPLING RESULTS AT TI-CO AIRPORT JANUARY 1975 TO DECEMBER 1975		56
7	FLORIDA DER SAMPLING RESULTS AT TI-CO AIRPORT JANUARY TO JUNE 1976		57
8	FLORIDA DER SAMPLING RESULTS AT MERRITT ISLAND APRIL 1974 TO JUNE 1976	. .	58

Figur	<u>e</u>	Page
9	FLORIDA DER SAMPLING RESULTS AT TITUSVILLE DECEMBER 1974 TO JUNE 1976	59
10	MONTHLY AVERAGES OF PARTICULATES AT MERRITT ISLAND, TI-CO AIRPORT AND TITUSVILLE; SO ₂ AT TI-CO AIRPORT	60
11	POPULATION DENSITY IN KSC AREA	61
12	AN EXAMPLE OF HC1 AND ACID RAIN SENSOR SITING	62

SUMMARY

This report describes an air quality monitoring network designed to characterize the perturbations in the ambient air quality in the region surrounding Kennedy Space Center (KSC) during space shuttle launch operations. An analysis of cloud processes and prevalent meteorological conditions indicates that in some instances the transient levels of HCl deposition from the shuttle ground cloud can be a cause for concern. The system designed to assess this impact would sample HC1 and acid rain with a reasonably extensive network of inexpensive sensors; the samples thus collected would subsequently be subjected to laboratory analysis at a central site. Although a comparison of shuttle emissions with other area pollutant sources indicates that there will be minimal long term impact on the existing overall air quality (which is characterized by low pollutant levels) it is nevertheless recommended that a quantitative measure of these effects be obtained via the long term limited monitoring of NO_x and particulates. Further recommendations call for all monitoring activities to be confined to KSC property, although the HCl network could easily be expanded beyond the periphery.

I. <u>INTRODUCTION</u>

Concern over the environmental impact of the space shuttle launch operations has prompted a concentrated effort by NASA directed at determining the physical, chemical and dynamic properties of the rocket effluent cloud left in the troposphere after launch. In conjunction with these studies, an effort is being made to assess the effect on the local environment of this exhaust cloud. If it appears that the toxic cloud has an adverse effect on the local environment, certain launch constraints may be imposed on shuttle operations.

The purpose of this report is to define the requirements of an air quality monitoring network needed to characterize the perturbations in the ambient air quality in the region surrounding Kennedy Space Center (KSC) during shuttle launch operations. The goals are to establish the nature and extent of a monitoring network necessary to perform the following functions:

(i) provide pre-launch ambient data that can be used in conjunction with ground level deposition predictions from cloud diffusion models to help predict short term impact of a given launch, (ii) provide a means of monitoring the short term impact, and (iii) provide a means of monitoring the long term effects of shuttle operations on the ambient air quality. The system is not intended to capture peak ground level depositions of all pollutants from each launch, nor is it intended to provide input data to the cloud diffusion models.

This study is concerned solely with the effects of the space shuttle and hence, the pollutants of interest are those species that emanate from the rocket motor and/or result from interactions, if any, of these species with ambient pollutants. As such, no attempt has been made to define a system applicable to "institutional" monitoring, which involves an extended system designed to account for and monitor all possible pollutants in the area.

The specific problems addressed in this report concern which pollutants should be measured, what instrumental techniques should be employed, where the instruments should be located, and the cost of installing and operating the system. To solve these problems a detailed analysis of several pertinent factors has been made. Section II provides a description of the ground cloud at stabilization in terms of the species emitted

by the rocket motors. In-cloud processes that affect ground level pollutant deposition are described, as are the effects on cloud motion of various KSC meteorological conditions. Information obtained from past Titan launches and theoretical predictions made for the shuttle indicate the possibility that short term HCl depositions can be a matter of concern.

In Section III the existing air quality in the KSC area is defined, the emission sources identified, and the monitoring network operated by the Florida Department of Environmental Regulation is described. The small number of pollutant sources and the efficient atmospheric mixing combine to yield a very good ambient air quality.

Section IV describes the scenario for space shuttle launch operations and defines specific times in the countdown sequence when the launch director can act on advisory information on potential modifications to the ambient air quality that might result from a launch.

In Section V the measurement requirements are determined. The resulting system is designed to assess the transient impact of the shuttle ground cloud by monitoring HCl and acid rain with a reasonably extensive system of inexpensive sensors, samples from which would be analyzed at a central site. Although the results from Sections II and III demonstrate that there will be little or no long term impact of shuttle operations on ambient air quality, it is recommended that a quantitative measure of these effects be determined via the limited monitoring of NO_{X} and particulates. It is further recommended that all monitoring activities be confined to KSC property. The expansion of the HCl network to outside KSC property could easily be made if initial measurements show this to be necessary.

In Section VI, applicable measurement techniques are described that satisfy the requirements outlined in Section V. Instrument capabilities are not evaluated against the mission requirements listed in Section IV because it is extremely unlikely that measured pre-launch ambient air quality data will provide the necessary information with which to make decisions concerning launch constraints.

Section VII provides recommendations for the monitoring systems, including specific instrument types and costs. The recommended HCl detector systems require some further development to increase their capabilities and

their applicability to the specific requirements for monitoring the ground cloud.

The author would like to acknowledge the valuable contributions made to this program by W.J. Miller on the interaction of ground cloud and pollutant species, B.C. Hwang and R.K. Gould on the ground cloud description, and A. Fontijn on HCl monitoring techniques.

Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

II. DESCRIPTION OF GROUND CLOUD

A. COMPOSITION

The cloud formed in the troposphere* during the launch of space shuttle will be broken into several segments by wind shear. The parts below the inversion layer which contain entrained air, dust and any sprays of water and/or neutralizing agents which remain airborne in addition to the solid rocket booster (SRB) and orbitor engine exhaust products, move and disperse within the turbulent planetary boundary layer. In this report, this lower portion of the cloud is referred to as the ground cloud. The exhaust products include HCl, Al_2O_3 , H_2O , CO_2 , N_2 , NO_X , Cl_2 and a large variety of minor species. Table I lists (i) concentrations of species exiting from the rocket motors, 1,2 (ii) the same weight fractions following the afterburning due to the entrainment of air in the plume, 3 (iii) the range of masses of these products contained in the stabilized cloud, and (iv) the total masses of materials up to 10 km. Item (iii) covers the prevalent situations in which the cloud stabilizes at an altitude between one and two km and is calculated assuming burn times of 15 to 24 sec.

In addition to the exhaust products listed in Table I, the ground cloud contains large amounts of debris swept up at the launch site. In the 0.01 to 1 μm particle size range, the mass of particles is quite high compared to that of alumina, the principal particulate exhaust product. Several minutes after launch the total particle mass in this size range has been observed (unpublished data from G. Gregory, NASA/Langley Research Center) to be generally 10 to 15 times that of alumina. It may be considerably greater than this initially before sedimentation rapidly removes the larger ($\geq 50~\mu m$) sized debris particles swept up by the cloud. The composition of debris is not known but is almost certain to include NaCl, ferro-silicates, and other soil species. This debris may be responsible for carrying HCl (by sorption) and alumina (by particle scavenging) from the exhaust to the ground near the site.

^{*} The troposphere is taken to extend to 15 km altitude.

Another important constituent of the cloud not included in Table I is the large amount of water in the air entrained by the cloud. However, partial entrainment of the deluge water, injected in the flame trench at about 20,000 kg/sec, and the orbitor exhaust are included.* Figure 1 shows cloud volume (and vertical velocity) as a function of time for the May 20, 1975 Titan III ground cloud. The space shuttle cloud is expected to be similar in most respects to this because the cloud volume is predicted (by one model) to be proportional to the heat content to the 1/4 power. The shuttle cloud heat content is approximately 2.3 times that of the Titan III. Figure 2 gives the observed height of the cloud as a function of time for several Titan III launches.

B. PROPERTIES AT STABILIZATION

The lower portion of the Titan III exhaust cloud generally stabilizes at altitudes in the range of one to two km. At this time in the cloud's history, the composition depends heavily on the amount of air that has been entrained (the dilution ratio). Table II shows the cloud composition at stabilization for the exhaust products given in Table I. The dilution ratio is 5000:1 which approximates the case of the December 10, 1974 Titan III launch which had the lowest cloud dilution at stabilization of all the Titan cases analyzed. For other Titan launches, the cloud dilutions varied up to five times this value which would result in correspondingly reduced species concentrations in the stabilized cloud. Prior to stabilization, the cloud properties are dominated by vehicle exhaust properties and the thermal stability of the environment. Subsequent movement and the rate of cloud dispersal will be governed by meteorological conditions.

A major mechanism by which the ground cloud affects the area near the launch site is via deposition of acid (chloride) aerosols from the cloud. The growth and sedimentation of these aerosols involves (i) a dry deposition process in which the large size fraction of the exhaust particulate and debris swept up during launch settles to the ground, (ii) condensation of an acid

^{*} However, the amount of H₂O in the cloud contributed by the rapid mixing with a large amount of ambient air completely dominates H₂O from the vehicle.

mist which may occur after the cloud cools to near ambient temperatures in situations in which the relative humidity is sufficiently high, and (iii) washout of cloud components by an overriding rain.

The dry deposition process in which exhaust particles (alumina) and debris settle to the ground can result in some deposition of chloride. HCl is sorbed on the exhaust alumina (and may sorb on debris as well depending on its composition and solubility). It is roughly estimated that on the order of 5% of the HCl in the cloud is sorbed on alumina. The average alumina particle radius a short time (several minutes) after exiting from the rocket motor is \approx 0.05 μm . This information, combined with that of Table I, indicates that between one and three monolayers of chloride are formed on the particles. small size of the exhaust particles and the fact that it is the smaller of these which have a very large surface to volume (mass) ratio means that agglomeration of these fine particles to larger alumina and debris particles is the dominant mechanism by which chloride can be transported to the ground. Calculation of the rate of agglomeration and sedimentation indicates that, during the cloud rise, about 0.05% to 0.5% of the chloride in the cloud can be carried to the ground by the dry deposition of alumina. Deposition of 1 to 10 mg of chloride per m² ground surface area results, assuming a projected area of ≈.1 x 10⁷ m² under the cloud at stabilization.

As the cloud approaches ambient temperature, particle growth via condensation of HCl and water may occur if the humidity is sufficiently high. For HCl/ $\rm H_2O$ systems relative humidities of $\geq 80\%$ are required for nucleation and droplet growth; however, in the presence of extremely hygroscopic particles, growth via condensation may occur at lower humidity. The occurrence of condensation/ growth and its enhancement of deposition at the ground has not been calculated.

A major problem may arise from washout of HCl by an overriding rain. In the worst case, in which HCl is present in the cloud only as a gas, the pH of raindrops passing through the cloud initially can reach very low (< 1.0) pH values. The rate of HCl deposition in this case depends on (i) the cloud volume and thickness, (ii) the time in the cloud's history at which rain starts, and (iii) the rate of rainfall. A straightforward model by Pellet can be used to predict the pH and HCl deposition rates in this worst case.

C. CLOUD MOTION

The size, motion, and rate of deposition of the ground cloud after cloud rise is determined by meteorological conditions at and around KSC. In this section these cloud properties for each of the more common meteorological conditions are discussed. The probability of occurrence of various wind directions is given in Table III as a function of month. (These results have been interpreted from unpublished synoptic data of Siler, Johnson Space Center.) To predict cloud behavior, in addition to the general synoptic conditions, such details as wind field near and above ground, turbulence properties, temperature and humidity must be known. The discussion here will emphasize the most important of these, viz., turbulence properties and wind direction.

1. Upper Cloud

That portion of the stabilized cloud lying above the planetary boundary layer behaves in a manner dictated by the synoptic (large scale) meteorological weather patterns. Of the wind directions which result from these patterns, only cases in which there is an easterly wind or land/sea breeze situation (see Table III) can be expected to cause problems. other cases, the cloud travels out to sea. In most situations at KSC, the higher portion of the cloud will initiate formation of a larger cloud presumably due to condensation on exhaust particles. Whether or not these clouds result in rain and where it travels is not yet well understood. clouds will not affect the ground unless they cause rain, there is an overriding rain, or a local circulation brings them back to the ground. In any case the impact would be far from the launch site.9 In a sea/land breeze cycle the sea breeze situation will occur during the day. In this case the upper cloud can deposit material on the ground if a storm is induced by the sea breeze. 10 (It has also been speculated that exhaust products may accelerate storm formation. 11) At night the land breeze, which is much weaker than the sea breeze, can cause problems only if later developments on the synoptic scale cause rain inland.

2. Lower Cloud

The behavior of the lower portion of the cloud depends on details of the turbulent structure near the ground but some general conclusions may be In the daytime a pollutant deposition pattern on the ground will follow a path which will generally be within 35° to 50° of that of the synoptic scale wind direction. At night this path will lie closer (± 20°) to the direction of the geostrophic wind. 12 Therefore, only the sea breeze and the easterly synoptic patterns are of concern. From studies conducted to date it is found that generally late in the afternoon, when the inversion layer begins to dissipate, the ground wind direction cannot be predicted. In this case southerly and westerly synoptic wind conditions may cause problems by inducing easterly ground winds. Also, because in this case turbulence is often low, cloud dissipation is slow and large HCl concentrations may reach the ground due to the resulting descending convection. In the late afternoon the inversion layer thickness increases and this also may force the ground cloud to the ground. Lack of far field measurements under these conditions and the lack of any model capable of treating this situation prevent assessment of the seriousness of this possibility.

From recent model predictions made for a variety of hypothetical meteorological conditions (reported in Ref. 13), the maximum peak concentration of HCl at ground level reached 4 ppm within 7 km of the launch site. These calculations were made using the MSFC/MDM code following procedures outlined in Ref. 14. It has been shown experimentally that this model consistently overpredicts HCl deposition¹³ and that actual results will not approach these high values.⁴ Figures 3 and 4 show examples of maximum ground level concentrations and dosages for a typical summer, sea-breeze situation. The calculations were made using the MDM¹⁴ and DISF¹² models. The results are quite different, with the DISF model predicting lower maximum concentration and dosage occurring farther from the launch site. More discussion of the various model capabilities can be found in Ref. 4. In no model calculations do the concentrations of NO_X, Cl₂, CO or particulates exceed allowable limits.⁴, 13

3. Weather Patterns

When the synoptic scale is strong (there are large pressure gradients) it will dominate and there will rarely be smaller or mesoscale patterns. However, with weak synoptic effects, the mesoscale patterns induced by the land/sea breeze cycle create higher levels of turbulence, thus increasing the thickness of the planetary boundary layer. In addition, these mesoscale patterns control the move-The sea breeze is often strong and may penetrate 20-30 km inland. ment of storms. Land breezes occurring at night are much weaker than sea breezes and generally the land breeze circulation pattern penetrates inland only 10 km. Within the planetary boundary layer two situations may arise during the daytime. situation is that in which an inversion layer is present. This layer grows from the ground in early morning and at 10AM to 12PM may reach a thickness of one to In the afternoon the planetary boundary layer thickness remains constant but the turbulence levels decrease. Turbulence near the ground in the late afternoon will become weak and correlations between large scale wind patterns and wind patterns at the ground will also become weak. In the second situation no inversion layer exists; little is known about the turbulence structure in this situation. However, in some cases the turbulence (the planetary boundary layer) may extend as high as 8 km but in other cases the turbulent layer near the ground may be only a few hundred meters thick. At night there will generally be a thin stable layer near the ground. In summary, the thickness of the planetary boundary layer at KSC is highly variable and quite difficult to predict.

III. AMBIENT AIR QUALITY AND MONITORING PROGRAMS IN EAST CENTRAL FLORIDA

A. SOURCES OF POLLUTANTS

The ambient air in the region surrounding KSC is relatively clean due to the small number of pollutant sources and the efficient atmospheric mixing characteristics of a region whose microclimate is controlled by the land/sea interface. Pollutant emissions in Brevard County are dominated by the Florida Power and Light power plant at Frontenac and the Orlando Utilities Commission power plant three km to the north near Bellwood. These plants are on the west shore of the Indian River roughly 22 km from the shuttle launch Orlando Utilities burn no. 6 fuel oil with a sulfur content of 1-2% and plan to burn 3% sulfur fuel in the future. Florida Power and Light burns low sulfur fuel oil (<1%). Both plants also burn natural gas. Emission data for these plants were obtained from the National Emission Data System through the Florida Department of Environmental Regulation (DER) in in the form of annual estimates based on plant capacity, fuel used, percent of time in operation for individual units, etc. This system lists by county estimated (in some cases measured) emissions from all sources of consequence in the state. The power plant estimates are provided by the power companies themselves, and are based on industry and EPA standard formulas that relate emissions and amount (and type) of fuel consumed. pollutant sources in this area are asphalt plants (some asbestos), cement plants (alkaline earth bases such as Ca(OH)₂), and agricultural burning. emission estimates for the industrial sources are shown in Table IV. 1976 estimates for the power plants are shown in Table V.* No data were

^{*} The discrepancy between the 1975 and 1976 estimates for Orlando Utilities may be due to the fact that the largest of their three units was out of operation for several months resulting in abnormal operation of the plant for that period.

acquired for agricultural burning but it is believed that it does not constitute a major impact on the ambient air quality.*

B. AIR QUALITY STANDARDS

The applicable air quality standards for NO_2 , particulates and SO_2 in the east-central Florida area are the secondary National Air Quality Standards shown in Table VI. These standards are more stringent than the primary standards and attempt to protect the general public from any known or anticipated adverse effects of a pollutant. The limits for HCl exposure are those given by the Advisory Center on Toxicology on and are shown in Table VII.

C. FLORIDA STATE MONITORING SYSTEM

Environmental monitoring in east central Florida is handled by the Orlando office of the DER whose responsibility extends to Orange, Osceola, Seminole, Lake, Indian River, Volusia, Marion, and Brevard Counties. They operate stations to monitor particulates, NO_2 and SO_2 . The particulates are measured by Hi-Vol sampling and are analyzed for total mass, not size distribution or particle composition. SO_2 and NO_2 are monitored using wet chemistry methods. The raw data from the various stations are sent to a central processing station in Tallahassee and then, in reduced form, to the EPA Region IV data bank in Atlanta. In addition to these stations, the agency has recently acquired a mobile station from EPA equipped with a Beckman 6800 gas chromatograph to monitor CO, CH_4 and total hydrocarbons, a Bendix automatic sulfur analyzer for sulfates, and a Malloy chemiluminescence monitor for O_3 and NO_X .

The measurement network is designed to place the monitoring stations near pollution sources such as power plants, airports and in cities. As such, they do not serve as background monitoring stations in the sense described in the World Meteorological Organization standards for ambient air

^{*} A recent situation in Lakeland helps justify this conclusion. A ban on agricultural burning had been temporarily lifted due to cold weather. The Florida DER operated their local particulate monitoring equipment during the burning and reported a nearly insignificant change from pre-burning readings.

quality monitoring 17 but tend to monitor areas with the highest pollutant loadings. Three sampling stations are located in Brevard County within 35 km of the shuttle launch sites. Particulates, $NO_{\rm X}$ and $SO_{\rm 2}$ are measured at Ti-Co Airport, while at Merritt Island and Titusville only particulates are measured. In addition, Florida Power and Light monitors particulates, $NO_{\rm 2}$ and $SO_{\rm 2}$ in the area. The locations of these five monitoring stations are shown in Fig. 5.

The results and statistical analysis of the data gathered at the DER stations are shown in Figs. 6-9. Plots of the 1975 monthly averages for particulates for Ti-Co Airport, Merritt Island and Titusville, and SO₂ for Ti-Co are given in Fig. 10. All the data indicate the levels of NO2 and SO2 are quite low. Particulates, however, are present in quantities that approach or (rarely) exceed the annual geometric mean standard of 60 μg m⁻³ (but not the 24 hour limit). This region of Florida is, however, one of the cleanest regions in the country with respect to particulates, 18 and these high (relative to SO_2 and NO_2) levels are most likely due to ocean salts. A sample of results of individual measurements taken at Ti-Co Airport is shown in Table VIII. Only the SO₂ data taken at Ti-Co show significant levels with respect to the annual mean, but with considerable scatter in the data. Particulate data from the stations operated by Florida Power and Light agree with those from the DER stations but Florida Power and Light had not employed proper sampling procedures with respect to temperature compensation in the SO2 and NO2 measurements, so comparisons of these data are meaningless. This problem has since been corrected.

In summary, the air quality in east central Florida is very good. The major emission sources that are present (the power plants) are compared with the shuttle in Section V to help assess the monitoring needs for the space shuttle program.

IV. SPACE SHUTTLE LAUNCH SCHEDULE

One of the functions of the monitoring system is to provide the launch director with advisory information on potential modifications to local air quality at key times in the countdown sequence. The long range plans call for a two hour countdown with hold points scheduled only after the countdown Predictions of adverse weather conditions may be disregarded has begun. until T-2 hours at which time the pad will be cleared and the fuel loading operation will begin. There will be a hold at T-45 min. before the crew will ingress but the primary hold point is the range safety "go for launch" at T-9 min. Current plans indicate that the initial assessment of launch success will be made at the T-2 hr. mark and therefore inputs to the launch director concerning possible adverse air quality modifications should be made at this time before the cryogenic fuel loading is initiated. Although launch holds can occur at less than T-9 min. for weather problems, the economic factors associated with launch constraints at this late stage of the countdown sequence are substantial.

It is expected that the two hour countdown will not be implemented until some time after operations begin. For the first several flights a four or five hour countdown will be used with several holds for engineering evaluation of various systems. The hold points in these cases will occur at the same operational points as in the two hour countdown, e.g. T-5 hrs. for fuel fill and T-2 hrs. for crew boarding. The T-9 min. hold for range safety will remain in effect.

V MEASUREMENT REQUIREMENTS

A. OVERVIEW OF AIR QUALITY MONITORING

1. General Considerations

In the most general sense air monitoring is a requisite for generating the data base necessary to assess air quality trends and pollutant interactions, determine the effects of air pollution on the environment, develop and enforce control regulations, and activate emergency procedures to limit or prevent pollution episodes. Within the framework of these general goals, various objectives can be realized by different monitoring systems. For example, long range global trends are monitored with systems situated far from any localized sources (natural or manmade); this type of network is concerned with global air quality at the local level and is intended to avoid monitoring fluctuations caused by local sources. Regional monitoring systems are more responsive to sources in a given demographic or geographic area, and, in principle, can be tailored to monitor the air pollution effects encompassing as large or small a geographic area as desired.

2. Specific Considerations for Space Shuttle

The system required for monitoring the effects of the space shuttle is representative of the most specific type of monitoring system, that of the single source. The monitoring network to be used in conjunction with launch operations must fit within a program that predicts cloud movement and pollutant fall-out prior to each launch, and measures ambient air quality prior to and after a launch. If the situation warrants, pre-launch data can be utilized in a number of ways. For example, if background pollutant levels are such that when added to predicted ground cloud deposition an unacceptably high dosage of that pollutant results, launch constraints may be implemented. Also, such data can be used to assess the effects of launch operations by comparing it with post-launch data either on a short term "cloud passage" or long term "effect on ambient" basis. Pre-launch ambient air quality data can also be used as input to diffusion models that account for the interaction of source and ambient species.

Post-launch measurements could be utilized in the following ways: In the short term, the network could provide the data necessary to monitor the

transient impact in a critical area of the cloud passage by comparison with pre-launch data. Also, the data can be useful in evaluating the performance of the cloud diffusion models if the cloud and/or predicted cloud passage is near a monitoring station. The long term data are important for determining the overall effects of shuttle operations on the ambient air quality.

The above performance requirements of the monitoring system require different though not necessarily exclusive capabilities. The measurement of pre-launch and long term ambient pollutant levels will require instrumentation with high sensitivity and stability. Short term, transient measurements require wide dynamic range and fast response time. For example, to monitor transient cloud impact and assess model performance, the measurement of HCl is most critical. On the other hand, for purposes of long term assessment of shuttle operations, all pollutant species in the cloud that could play a role in environmental impact should be monitored.

B. MONITORING REQUIREMENTS FOR KSC

In order to determine the specific requirements for efficient shuttle ground cloud monitoring at KSC, consideration has been given to the factors pertinent to the pre- and post-launch, short and long term measurement criteria listed above. The specific questions addressed are: (i) Does the cloud represent a large perturbation on the ambient air quality? (ii) What, if any, are the major reactions with ambient species? (iii) Where should the monitoring effort be placed, i.e., on pre- or post-launch capability? The answers to these questions will determine what species should be measured. Instrument siting considerations will be treated separately.

In order to determine the magnitude of the pollutant source represented by the ground cloud, comparisons were made with the pollutant loadings of the other major sources in the area, i.e., the two power plants on the Indian River, (see Tables IV and V). The annual input to the troposphere from the shuttle was estimated assuming 40 launches per year and the exhaust composition given in Section II. The results shown in Table IX indicate that the space shuttle ground cloud does not represent a large perturbation on the local ambient air quality when compared to the stack emissions of the local power plants although the particulate emissions are higher. Since the power

plants have a minor impact as evidenced by the available state monitoring data, it can be justifiably assumed that the space shuttle ground cloud will not present any long term hazard to local ambient air quality.

Although the ground cloud does not appear to present any long term ambient air quality problems, the short term transient impact during cloud passage can represent a large air quality perturbation. As indicated in Section II, ground cloud depositions of HCl can be significant. This short term problem can be aggravated if undesirable reactions of ambient species with ground cloud species take place.

The most obvious interaction of the rocket exhausts products with the ambient is afterburning, which increases the amounts of $\rm H_2O$, $\rm CO_2$ and $\rm NO$ in the exhaust cloud in comparison to the nozzle exit values. This process takes place before cloud rise. In cloud rise and at stabilization (with the cloud cool) the next most obvious effect is the formation of aqueous HCl from the interaction of gaseous HCl with $\rm H_2O$ in the exhaust products, and (in much larger quantities) from the entrained air (see Section II). Other effects concern reactions among $\rm NO_X$, $\rm SO_2$, $\rm O_3$, and hydrocarbons (HC). NO in the exhaust cloud is converted to $\rm NO_2$ via

$$NO + O_3 \rightarrow NO_2 + O_2$$
 (1)

or
$$2NO + O_2 \rightarrow 2NO_2 \tag{2}$$

depending on the dilution ratio and local concentration of O_3 . An increase in the NO_2 concentration greatly enhances the oxidation rates of other air pollutants frequently with undesirable local effects. The reaction that initiates this process is photolysis of NO_2 which occurs in the presence of visible and near ir light, i.e.,

$$NO_2 + hv \rightarrow NO + 0 \tag{3}$$

$$M + 0 + 0_2 \rightarrow 0_3 + M$$
 (4)

A balance is struck in the atmosphere between these two reactions and other 0_3 consumption reactions. The reaction with NO recycles the process via Reaction (1).

The O_3 however, is a highly active oxidizer and although it is not an exhaust cloud species per se it is increased dramatically through the above

reaction sequence. Potentially significant effects include the oxidation of HC via

$$O_3 + HC \rightarrow RO$$
 (organic oxy-radicals) (5)

which is the first step (or among the important first steps) in classical photochemical smog production. NO_X is the other essential reactant but it, too, is present in the exhaust cloud. Thus if an air mass with high O_3 levels encounters auto exhausts or other hydrocarbon emissions, local photochemical smog could result. Another consequence of increased NO_2 and O_3 concentrations is the oxidation of SO_2 (e.g., from power plants) in humid atmospheres, producing H_2SO_4 . A third possibility is the interaction of NO_X and O_3 on condensed phases to produce nitric and nitrous acids.

An examination of the above chemical systems within the context of prevailing KSC atmospheres indicates that interactions of the cloud and ambient species are not likely to produce important adverse environmental impact due to the characteristic low levels of pollutants in the area. The key step in the interaction mechanisms is the production of O_3 . However, the levels of NO_X in the KSC area power plant plumes are considerably higher than that in the ground cloud and yet no significant smog problems now exist in the area (private communication from R. Garrett, Florida DER, Orlando). Similarly, other acid aerosol production will also be small due to low ambient levels of SO_2 and NO_2 . If any were formed, they would be completely dominated by the HCl in the cloud. Hence, it is concluded that there will be no appreciable interaction of ground cloud constituents with ambient species, mostly due to the lack of ambient pollutants.

C. MONITORING GOALS

The recommended monitoring system should serve three functions: (i) It should establish a baseline of data prior to the start of shuttle operations that can help serve as a basis of comparison for future data; (ii) it should have the capability of characterizing the transient, short term impact of individual launches; and (iii) it should yield a quantitative measure of the long term effects or lack of same due to shuttle operations.

It is re-emphasized here that this study is addressing the monitoring requirements that are applicable to <u>space shuttle effects only</u>. No attempt is being made to define monitoring systems applicable to any other NASA functions at KSC or to satisfy the requirements of environmental statements that concern the KSC industrial complex as a whole.

Short Term

Two direct objectives of monitoring systems directed at characterizing the effects of individual launches are: (i) to provide pre-launch data that would aid in pre-launch cloud movement predictions and (ii) to provide post-launch data that would describe the transient environmental impact of the ground cloud.

The MSFC/MDM diffusion code¹⁴ uses meteorological inputs near the launch site to make downwind cloud deposition predictions. This model does not account for reactions with ambient species and cannot utilize inputs (such as wind speed or direction changes) along the predicted path without restarting the calculation. Hence, no additional pre-launch downwind measurements would facilitate better model predictions than those which are currently possible.

As far as post-launch conditions are concerned, HCl presents the most serious problem. HCl will be deposited in the atmosphere mostly in the gaseous state but depending on weather conditions, can rainout as an aerosol mist in high humidity situations, or washout in an overriding rain. Although Titan III data⁵ and model predictions for the shuttle⁴ indicate the maximum allowable human dosage of HCl may not be reached (see Section II) the gaseous deposition may still reach levels irritating to humans and damaging to some forms of vegetation. Also, as discussed in Section II, the initial stages of an overriding rainfall can scavenge large amounts of HCl and produce highly acid rain. Hence, the post-launch monitoring of HCl and local rain acidity are critical parts of the recommended program.

Long Term

Although the evidence suggests that no other cloud species will create an environmental hazard, it is prudent from a legal perspective that NASA have the capability of demonstrating that this is in fact the case. In order to achieve this goal, it is recommended that NO_{X} and particulates be monitored. NO_{X} , though not present in large quantities in the cloud, is a

highly undesirable pollutant in its own right, and is easily and accurately monitored. Particulates are present in large quantities in the cloud, as well as in the ambient, and participate in the HCl scavenging process. Since the particulates in the cloud are mostly dust and debris kicked up during launch and entrained into the cloud during cloud rise, it would be useful to have particle composition analysis capability in addition to mass concentration measurements to determine the partitioning of shuttle produced and ambient particulates in the cloud.

In order to determine long term air quality perturbations, a solid baseline should be established. This baseline could be created by operating the recommended system for a period of time prior to the initial launch, e.g., one year, and by the utilization of data presently available from the Florida DER sampling program. In addition to helping provide the necessary baseline, data from the DER stations (and the power company stations) could be used to assess the local perturbations of NO_{X} and particulates due to the shuttle by providing a means of compensating for large scale trends in ambient levels of these pollutants. It is therefore recommended that lines of communication remain open between KSC and the Florida DER so that KSC can utilize all the available data generated by the DER and the utilities both prior to and after shuttle operations begin.

3. Airborne Sampling

A possible effect of particulates in the ground cloud may result from the interaction of these particles with small scale meteorological patterns that affect local rain systems. Also, more information would be desirable on the particle composition and source identities in the cloud and on the HCl/particulate interactions that affect acid aerosol growth and the scavenging of acid mist or chlorinated particles. Pertinent measurements in this case require airborne sampling. Although a program of this type may be construed as a research project (which is not the intent of these recommendations) such measurements should be made, at least for the first several launches, because of the ultimate relationship of this data and these processes to the impact of the shuttle on the ambient air quality.

D. MONITOR SITING

The siting of instruments for any specific application depends on the overall objective of the program. In this case the monitoring of the transient impact of the cloud, i.e., HCl monitoring, requires different considerations from the determination of the long term effects through the measurement of NO_X and particulates.

1. HC1 Detectors

To determine the transient impact of the shuttle ground cloud one could deploy mobile "cloud chasers", initially directed by modeling predictions to locate the monitoring equipment in the cloud path. This method, if properly executed, would enable a large number of measurements to be made to characterize in detail the HCl deposition of each launch. Another approach is to "blanket" the area with inexpensive HCl monitors to give a reasonable probability of accounting for a given launch and to monitor critical areas, e.g., population centers and certain agricultural areas.

We recommend the latter approach for HCl monitoring with enough monitors to satisfy both requirements. This decision is based on the fact that the operation of mobile stations is likely to be expensive from the standpoint of manpower and equipment required and the choice of instrument sites is, of necessity, limited. The utilization of fixed position sensors does require a manpower investment in placing and retrieving the sensors, but only those that have been exposed to the cloud need be routinely analyzed. In addition, more versatile siting is possible.

The locations of the monitors depend on the projected range of high HCl fallout and the areas within this range which are likely to suffer adverse effects from such fallout. Titan III measurements and shuttle predictions using diffusion models (see Section II) indicate that maximum ground level depositions occur from 5 to perhaps 20 km from the launch site. The closest populated region, Titusville, lies 20 km to the west. Other populated areas in the KSC area are shown in Fig. 11. The models that predict maximum dosages to lie far (e.g., 20 km) from the launch site also predict low values for this dosage; models that predict high dosages show the deposition to occur much closer (e.g., \sim 5 km (see Figs. 3 and 4)); it is not possible to state

with authority at this time that no populated areas will be affected by HCl deposition. However, it does appear unlikely that any populated area will be subjected to dosages or concentrations that approach dangerous levels. The probability is higher though that orange groves on KSC property (see Fig. 11) which are leased to private growers could be subjected to high dosages of HCl. Some of these groves lie 7 to 10 km from the launch site and could be damaged by the HCl, resulting in financial losses to the growers.

With these factors in mind, it is recommended that the HCl monitors be confined to KSC property, with the highest density of instruments located at the sections of the periphery near the closest populated areas. Other sensors should be placed in the interior of the property to monitor dosages on the orange groves. Since at times there may be a large number of visitors on the base to witness launches, it may be advisable to have some monitors near the roadways with the highest concentrations of spectators. If it appears, after launch operations are underway, that HCl monitoring should, for the sake of public welfare, be carried out outside KSC property, it would be an easy task to extend the monitoring network to the required areas. The actual number of sensors selected is a compromise between the cost of the equipment and the resolution of the network. The costs for various network arrangements are outlined in Section VII.

2. Acid Rain Monitors

An acid rain network can be viewed as both a short and long term system. A network set up to give good spatial resolution with respect to any acid rain resulting from ground cloud HCl washout can certainly provide long term data as well. As with HCl monitoring, a large number of inexpensive collectors can be located in the KSC area and could be easily expanded if required. The existence of an extensive meteorological measurement network at KSC should make this an easily implemented task.

3. NO_x and Particulate Monitors

The siting criteria that must be met for NO_{X} and particulate monitoring are quite different from those of the HCl system. Because the purpose of this system is to determine if there are any long term effects on

the ambient air quality, rather than to establish short term effects, fewer instruments need be employed. Since it is not the purpose to "catch the cloud" after each launch, the major objective is to isolate the system from direct effects of other sources. With the exception of the two power plants 22 km from the launch sites, the area is generally free of pollutant sources and because of the constant atmospheric mixing due to the local meteorological conditions the ambient air quality is relatively homogeneous. Because of this and the evidence that suggests negligible long term effects of shuttle firings on the ambient air quality, only a very few monitors will be needed. These monitors could be located in almost any source-free area within the KSC boundaries, e.g., away from roads or KSC complex power plants.

E. SUMMARY OF MEASUREMENT REQUIREMENTS

The monitoring of HCl deposition is the most crucial aspect of the recommended program. To provide an assessment of the short term impact of shuttle launches, a large number of inexpensive sensors should be located within KSC. Acid rain should also be monitored with an extensive, inexpensive system to yield both short and long term environmental impact data. Other long term monitoring should be performed by measuring ambient NO_X and particulate levels. The acquisition of baseline and impact data in this case requires only a small number of instruments.

VI, CANDIDATE INSTRUMENT SYSTEMS

In this section, various types of instrumentation which satisfy the criteria set forth in Section V will be discussed. An evaluation of the instrument capabilities against the mission requirements given in Section IV is not necessary since it is not envisioned that a situation would arise where pre-launch ambient air quality data could provide the information necessary to make decisions concerning launch constraints. From the discussions in the previous sections, it is apparent that the interaction of the ground cloud with ambient pollutant species is minimal. The only data by which meaningful predictions of the environmental impact could be made, prior to launch, is meteorological data.

A. HCI MONITORING METHODS

A large number of HCl measurement methods in ambient air have been proposed, some of which are operational and some still in development. These techniques can be classified into those that require off-site analysis, those that perform on-site analysis of collected samples, and remote sensing monitors. A summary of the characteristics of many of these methods can be found in reviews by Gregory 19 and Gaarder and Jensen. 20 Pertinent specifications for all the methods considered are given in Table X. Unfortunately the presently operational methods are either too expensive for multiposition monitoring or are incapable of unambiguously distinguishing ground cloud HCl from other constituents of the KSC atmosphere particularly SO2 and NaCl. the two most advanced techniques, one, the luminol chemiluminescence method, suffers from interference by SO₂ and (less bothersome) O₃ and NO₂. The other, microcoulometry, in which Cl is measured, is subject to ambiguities due to the considerable quantities of NaCl present in the KSC atmosphere; NaCl interference could possibly be prevented by the use of a suitable filter, or sampling technique. There are, however, a number of other methods in various stages of development which appear particularly suited to measurement of ground cloud HCl deposition.

1. X-Ray Fluorescence/Filter Method

This method has been described by Lorenzen.²¹ It is apparently in routine use by IBM for computer site selection. It is currently also being tested by Stevens, et al at EPA.

Samples are collected by flowing ambient air through two filters. The first removes particulates, such as NaCl, the second is impregnated with NaOH which traps HCl. The filters are then analyzed in the laboratory with an X-ray fluorometer which is specific for Cl. Hence the method should be interference-free. The sensitivity of the fluorometer to Cl is $0.17~\mu g/cm^2$. Thus, for a flow rate of $1~\ell$ /min through a filter 37 mm in diameter, the sensitivity is about 8 ppm-sec (approximately 300-fold below the NAS maximum dosage limit--see Section III). More development is needed to establish the maximum sensitivity, which is a function of pumping speed, filter area, and extent of HCl absorption on the particulate filter.

While the method appears well established, the acquisition cost of the X-ray fluorometer (about \$20,000) could be a disadvantage. However, as in other off-site analysis methods only one such instrument is required.

2. Modified Luminol Chemiluminescence/Sampling Tube Method

The modified luminol chemiluminescence method (private communication from R.H. Moyer, Geomet, Inc., Pomona, CA) is an adaptation to the ground cloud problem of the well-tested commercially available luminol chemiluminescence method. It is a total dosage method, which has been subjected only to preliminary testing.

Samples are collected with 45 cm long 0.2 cm i.d. alumina tubes,* coated with NaHCO3. The HCl reacts with this coating to produce NaCl; however, most of the ambient NaCl apparently flows through the tube without precipitating. Gas flow through the tubes is maintained at 2 ℓ min⁻¹ by vacuum pumps. After the launch the tubes can be collected for analysis at a central location. Analysis consists of conversion of the NaCl to Cl₂; the total amount of Cl₂ then

^{*} These coated inlets which make use of the tendency of HCl to adhere to inlet tubes (which plagued many earlier HCl measurement methods) represent the major advance of all these variants of the luminol chemiluminescence method.

is measured by one standard luminol chemiluminescence instrument. The analysis time required is about five minutes per tube. The specifications for this method are: (i) efficiency for interfering NaCl particle detection is 1%; (ii) the efficiency for HCl trapping and measuring is 95%; and (iii) the limit of HCl sensitivity is $5 \times 10^{-3} \, \mu \mathrm{g}$ (or 0.1 ppm-sec).

In a variant of this method the alumina tubes are coated with NaBr and NaBrO₃. As in the regular luminol HCl detector Br_2 is released in one tube and trapped as bromide in a second tube. After collection of the tubes, the bromide is converted to Br_2 which is again detected by its luminol chemiluminescence. This variant would appear to be a less desirable one because acid gases such as SO_2 would also release Br_2 resulting in interference problems similar to those of the commercial instrument. In the regular commercial HCl instrument O_3 and NO_2 also interfere due to their direct reaction with luminol. However, such cannot occur in the trapping system of the modified luminol method since the luminol here does not come into direct contact with the ambient.

3. Microcoulometer/Sampling Tube Method

This method, described in Ref. 19, is one whose sample collection technique is similar to that of the modified luminol chemiluminescence method above. Small (1 mm diam) capillary tubes are coated with dried NaNO₃ which traps HCl from a gas stream drawn through them. In the laboratory, the tubes are washed with a precise amount of distilled water, a small sample of which is analyzed for Cl⁻ via microcoulometry. The lower detection limit is about 10 ppm-sec; upper limits depend on tube dimensions. The method is still in the development stage.

4. Comparison and Summation

Of the techniques listed in Table X, the wet chemistry methods all suffer heavily from interferences. Because of the need for a large number of sensors, the monitors that perform on-site analysis represent a large capital expense. Remote monitoring methods, because of their expense and need for extended development are not recommended.

B. NO_X MONITORING METHODS

An overview of NO_{X} monitoring techniques is given in Ref. 15 and various methods are summarized in Table XI. A number of these methods satisfy the monitoring requirements described in Section V. NO_{X} monitoring methods consist of manual analytical techniques and automatic analyzers. Manual techniques usually involve wet chemistry analysis; some automatic analyzers are self-contained adaptations of these methods. These two broad classes are discussed below.

1. Manual Techniques

Manual monitoring methods generally involve the on-site collection and retention of a sample, and its subsequent chemical analysis, usually in a laboratory removed from the sampling site. When applied to ambient air analysis, where NO_{X} usually occurs in small amounts, large samples and/or sample concentration methods are typically required to bring the NO_{X} concentrations within the detection range of most analytical techniques. Methods employing concentration techniques, e.g., bubblers, usually sample continuously over a long period of time. This method, which is employed by the Florida DER in their sampling program, integrates over a specific time interval. For example, the Florida system samples for 24 hours every six days but for other applications, such as to define diurnal variations in NO_{X} , sampling times can be shortened.

2. Automatic Monitors

Automatic monitors obviate the need for laboratory analysis of samples and require less personnel involvement in their operation. Continuous analyzers allow uninterrupted output within certain integration times or processing delays, depending on the techniques used. Semi-continuous monitors repeat a sample-analysis cycle on a regular basis with the ideal case employing fast enough cycle times to resolve the shortest time scales of significant change.

Commercially available instruments operate on a wide variety of principles including colorimetry, ion-selective electrodes, amperometry, electrochemical cells, chemiluminescence, bioluminescence, and various

absorption spectroscopy methods (see Table XI). The most suitable of these instruments is the chemiluminescence analyzer that monitors, via a photomultiplier tube, the light produced by the reaction of NO with O_3 . Sensitive only to NO, they require NO_2 converters to enable $NO_{\rm X}$ measurements. Initially developed at AeroChem, ²² chemiluminescence analyzers are available from numerous manufacturers and offer the advantages of continuous read-out, fast response, high sensitivity (to less than 1 μg m⁻⁸), linear response over a wide dynamic range (up to 10^7 μg m⁻³), minimal interference and good reliability. The chemiluminescence method was designated the Federal Reference Method (FRM) for ambient NO_2 monitoring in 1976 by the EPA.²³

3. Comparison and Summation

Bubbler methods, though probably adequate from the point of view of sensitivity, do not provide continuous data output, but integrate over long periods of time. Hence, small scale fluctuations in NO_{X} concentration will not be resolved. This is not necessarily a drawback in a program designed for long term assessment of ambient effects of the shuttle, since this method is in wide use by the EPA. In addition, the hardware is inexpensive. On the other hand, the continuous output afforded by automatic monitors is desirable as is the high sensitivity of techniques such as the chemiluminescence method. Although the cost of automatic machines is higher, only a small number are needed and laboratory analysis is not necessary. Remote instruments, e.g., spectroscopic methods, are not recommended because in general they have low sensitivity, are expensive and have not been shown capable of providing ambient data which can be compared with confidence to data obtained via accepted procedures in other monitoring programs.

C. PARTICULATE MONITORING METHODS

Particulate monitoring methods can be separated into the categories of manual methods, automatic methods, in situ monitors and remote sensors. Manual techniques have long been in use and only in the last few years have more sophisticated monitors been developed. A comparison of particulate monitoring techniques is given in Table XII.

1. Manual Techniques

In all manual techniques, particles are removed from the ambient air sample and analyzed off-site. The major difference in the methods is in the manner in which the particles are removed from the air. The most widely used technique is filtration, whereby ambient air is drawn at a specified flow rate through a filter of high collection efficiency for particles with sizes as low as $0.3~\mu$. The filters are collected after a given sampling time and weighed to yield the total mass concentration of particles in the sampled air. This technique, known as high volume sampling (Hi-Vol), is the FRM for ambient monitoring of suspended particulates. A complete description of the method is available in Ref. 24. Chemical composition analysis can be performed on the collected sample if desired. Laboratory methods generally used include atomic absorption spectrophotometry, emission spectroscopy or X-ray fluorescence.

Inertial impactors can be used²⁵ to measure size distributions. The principle employed is that particles will continue moving in their original direction when the air stream in which they are carried is deflected, and impinge on prepared surfaces. An adhesive coating on the surface collects the particles. These impactors can be staged to cause higher velocity air flow in successive stages allowing the collection of progressively smaller particles. The size range collected is typically 0.5 to 50 μ . Chemical composition can be determined by the same laboratory procedures used in conjunction with Hi-Vol sampling.

Other manual monitors utilize electrostatic or thermal precipitation techniques.²⁵ In an electrostatic monitor, a particle is charged near the sample inlet and subsequently captured on a collection plate. In a thermal precipitator, a thermophoresis force due to an imposed temperature gradient causes the particles to be driven to a cold substrate. These methods are usually used for special sampling of fine particles for optical or electron microscope examination.

A major advantage of all these methods is that a permanent record of the sample is obtained. Disadvantages include the physical disintegration or coagulation of particles caused by their impingement on the filter or collection surface, and the inability of making continuous measurements.

2. Automatic Methods

Automatic monitors do not require laboratory analysis capability and allow continuous or semi-continuous measurements. Similar to manual techniques in collection methods, this class of monitors performs the analysis automatically at the sample site. Monitors with electronic readout allow transmission of results to remote locations.

One type of automatic monitor is the beta radiation attenuation technique. In this method, a collection system similar to that used in Hi-Vol samplers deposits particulates on a filter tape. Beta radiation transmitted from a source (e.g., C¹⁴) to a detector through the sample is attenuated by the particles. The transmittance depends entirely on the particulate mass concentration and is independent of particle composition or physical properties. The particulate concentration is read out directly as a function of beta attenuation and sample flow rate through the system. This method allows semicontinuous monitoring governed by the sampling interval which can be made as small as one minute. A modification to this instrument has been made to allow time resolved (to 1 hour) composition measurement via off-site X-ray fluorescence of the collection tape (private communication from S. Chansky, GCA Corp., Bedford, MA). It is currently being evaluated by EPA Region I.

Another available method for measuring mass concentration is the piezo-electric technique in which the mass of particles collected on a crystal changes its resonance frequency which, in turn, is related to the mass of collected particles.

For determination of elemental composition, the emission spectroscopic technique used in laboratory analysis can be employed in an automatic device in which particles are heated and their characteristic atomic emissions are monitored by a spectrophotometer. This technique is sensitive to particles as small as 0.1 μ and, in principle, particle concentrations can also be determined. This method is still in the development stage.

3. In Situ and Remote Monitoring

In situ and remote monitoring involves on-site analysis with no sample accumulation or collection. Either spatially integrated or point sampling is employed. Photometric methods measure the intensity of light scattered off

the particles which is proportional to the particle size. Available systems tend to be expensive. New developments such as Lidar show some promise for in situ and remote monitoring of stationary sources, but are still in development stages.

4. Comparison and Summation

In general, particulate monitoring depends on mechanical devices for particle collection and laboratory analysis to determine sizes, mass concentration and/or composition. The standard Hi-Vol method, impactors and beta gauge methods are suitable devices but no one technique yields concentration, size distribution and composition data. Recent developments in optical and other techniques will probably soon result in increased on-site capability and less emphasis on laboratory analysis. However, most of the new developments are not yet available.

D. ACID RAIN MONITORS

The measurement of rainwater acidity is straightforward. The simplest method involves the collection of rain in a suitable container and analysis with a pH meter, although a more detailed composition analysis, e.g., the determination of Cl, Na and S content is also useful as an aid in establishing the source of acidity. A sampling device that opens the container only for the duration of the precipitation is desirable to help keep debris and insects, etc., out of the sample. Such devices are already in use at KSC and are adequate for the task. As discussed in Section II, the initial rain falling through the ground cloud will be more acidic than subsequent rainfall and a slightly more complex system is required to allow the determination of the time history of rain acidity during the period of precipitation. Such a system requires a method to open and close containers at predetermined time intervals, but is basically similar to the above device.

Interferents for the pH measurements are any acids (or bases), especially $\rm H_2SO_4$. However, measurement of all rain occurrences allows the establishment of a baseline against which samples taken during a launch can be compared.

VII. RECOMMENDED MEASUREMENT SYSTEM

The recommended monitoring system has the goals of assessing: (i) the short term environmental impact of the ground cloud via the measurement of HCl and acid rain, and (ii) the long term impact through the measurement of NO_{X} and particulates. Consequently, the instruments employed and the sites selected need not be mutually dependent and decisions regarding their selection can be made separately.

A. SHORT TERM ASSESSMENT: HC1 MONITORING

1. Instrument Selection

As outlined in Section V, the monitoring of HCl requires an extensive system in order to ascertain the effects of individual launches. Monitoring using bubblers, sampling tubes, or filters all allow inexpensive sample collection with central analysis. Bubbler methods, however, are plagued by interferences. Therefore, the present recommendations call for sampling tube methods employing either luminol chemiluminescence, or microcoulometric analysis, or filter sampling employing X-ray fluorescence analy-Each of these techniques offers the combined capabilities of good sensitivity, specificity, and economically efficient operation (after the initial acquisition costs) that are not found in any of the other available methods. Unfortunately, these techniques are relatively new and none has received extensive testing for conditions pertinent to the ground cloud prob-However, with the first launch over a year away, there is sufficient time to allow the necessary development of any of these methods. We recommend then that NASA select the most promising technique (e.g., by competitive bid) and sponsor its development for the current application. Our preference at this time is the selective filter X-ray fluorometer technique. sons for this are (i) the X-ray fluorometer can serve a dual function and perform selected elemental particle composition analysis, and (ii) the refinement of the HCl collecting filters does not appear to present any more problems than the development of the other two methods.

2. Instrument Siting

The siting of the sensors should be such that a high probability of encountering the cloud exists. From Section II an estimate of the ground level projected area of the cloud at stabilization height yields a characteristic length of around two km. For sensors placed at the periphery of KSC near populated areas, a spacing of one to two km should assure a high probability of recording the HCl fallout. Sensors placed in the interior to monitor HCl near orange groves or roadways where high spectator densities are expected can also be arranged in a manner to assure uniform coverage. An example of sensor placement to satisfy these requirements is shown in Fig. 12. Specific locations, of course, depend on accessibility to operating personnel.

B. LONG TERM ASSESSMENT: NOX AND PARTICULATE MONITORING

1. Instrument Selection

For the reasons outlined in Section VI, the monitoring of NO_{X} and particulates does not require an extensive system. Basically, the amount of NO_{X} emitted is in small enough quantities compared to that from other sources that any long term impact will undoubtedly be negligible. Particulate emissions also, when compared to the high ambient levels due to ocean salts, will probably represent a negligible perturbation on the ambient air quality. Nevertheless, it is prudent that NASA have the capabilities of documenting any long term effects of the shuttle program on the ambient air quality. The measurement of NO_{X} and particulates, because the data can be compared with that taken by the Florida DER, can provide that documentation. It is therefore recommended that this monitoring be carried out. As discussed in Section V, the larger spatial scales involved in long term monitoring require only a small number of monitors due to the homogenizing effects of the atmospheric mixing in eastern Florida. In addition, it is not desirable to have the measurements dominated by unrelated local effects such as automobile traffic. It is therefore recommended that for this type of monitoring, the number of instruments need be no larger than two each for NO_{X} and particulates.

It is recommended that $\mathrm{NO}_{\mathbf{x}}$ be monitored using commercially available chemiluminescence instruments or those already in the possession of KSC. The

chemiluminescence technique is the Federal Reference Method for NO_2 and offers the advantages enumerated in Section VI. Especially useful in the present application is the continuous sampling capability which can yield information on the normal fluctuations of $NO_{\rm x}$ (e.g., diurnal variations, etc.). Data acquisition can readily be performed via chart recorders. In addition, since this is an FRM, data can be usefully compared with other $NO_{\rm x}$ data available from the state or from monitoring systems operated by the utility companies.

The selection of particulate monitors is complicated by the various parameters measurable; unfortunately not all can be measured with one instrument. For overall ambient air quality evaluation, mass concentration is the most appropriate and by far the most widely employed measurement. case of the shuttle ground cloud, as in many other air pollution situations, particulate composition and size distribution measurements are also desirable although difficult and expensive to obtain. However, the change in ambient size distribution due to the shuttle is likely to be minimal because (i) Al₂O₃ particles from the shuttle are not single-sized but are distributed over two or three orders of magnitude within the range of naturally occurring particle sizes, 6 and (ii) previous discussions indicate that the long term effects of the shuttle on total particle loading is minimal. Hence, it is believed that the effort involved in applying a difficult technique to routinely measure very small (if any) differences in ambient size distribution and correlating these differences with shuttle exhaust output would be excessive. It is recommended, then, that the particulate monitoring be limited to mass concentration determinations and that samples be taken with Hi-Vol samplers or their equivalent. This method is selected because it is the Federal Reference Method for mass concentration and, as with NOx, allows for meaningful comparisons with other available data. In addition, this method allows the maintenance of permanent records of samples which can be periodically analyzed for composition if desired or deemed necessary. Beta gauges yield time-resolved mass (and by analysis, composition) data but for long term monitoring, this additional capability does not warrant the increased costs (≈ \$10,000 per unit). Although all composition techniques mentioned in Section VI are viable, it is recommended that the composition be analyzed with an X-ray fluorometer to utilize equipment recommended for the monitoring of HC1.

2. Instrument Siting

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The instruments should be situated in an area of KSC not strongly affected by local sources and should be located reasonably far from each other. Protection from weather and access to electric power is required. Installation in buildings away from the effects of automobile traffic is desirable.

C. ACID RAIN MONITORING

The measurement of acid rain should provide both short and long term impact assessment capabilities. A system that provides adequate short term coverage, i.e., a high probability of encountering each event (an overriding rain) coupled with an efficient long term measurement system requires about 15 collectors of the type currently available at KSC. An example of collector siting is given in Fig. 12, with many located near the meteorological towers. Analysis should include both pH and composition determination.

D. AIRBORNE SAMPLING

Airborne sampling of the ground cloud can help provide better input data for the source terms in cloud diffusion calculations and give a better assessment of the nature of the particulate matter in the cloud. This sampling procedure does not provide direct environmental impact data, but rather information to aid in theoretical studies of cloud dynamics. It is therefore recommended that airborne HCl and particulate sampling only be carried out as a secondary activity, whose need should be determined by the requirements of theoretical modeling efforts.

E. SYSTEM COSTS

The initial costs for the monitoring program include equipment acquisition and installation costs. Annual costs include materials for sensor replacement or refurbishment, equipment maintenance, and salaries for staff to operate the system and perform data analysis. Many variables are involved and the actual costs will depend on the results of competitive bidding and the amount of inhouse vs. contracted work, etc. An example of these

costs is given in Table XIII for a system that utilizes the X-ray fluorescence technique for HCl monitoring. The figures do not include any instrument development costs and are based on a 40 launch per year schedule. For the HCl network, the sensor cost is estimated from required items such as sensor tubes, filters and holders, pumps, flow indicators, and batteries. setup involves the materials required for field placement of the units including some form of shelter. Operational expenses involve placing, retrieving, and refurbishing the sensors, and analyzing the samples. The acid rain monitors should require little maintenance but will require service at each rainfall. On-site data analysis and collector cleaning will maximize operator efficiency. For the NO_{x} monitors, routine maintenance necessitates weekly changes in filters, drying agents, and calibration and servicing of the Data collection involves the weekly retrieval of recorded monitor outputs. Maintenance on the Hi-Vol samplers should be low but operator time requirements are higher than with NO, monitors due to the laboratory methods that must be performed. In addition to the expenditures listed in Table XIII, a one year program to generate $NO_{\mathbf{x}}$, particulate and acid rain baseline data involves approximately one man-year of operator time.

The personnel requirements listed in Table XIII call for approximately three man-years annually to operate the system. Roughly 1.5 man-years of minimally skilled labor are needed to place and collect HCl and particulate sample filters and perform the acid rain analysis. 0.5 man-years of higher level personnel with chemical laboratory technician training are required to perform X-ray fluorescence analysis for HCl and particle composition, and particle mass concentration analysis. The staff scientist referred to in Table XIII is required to supervise the monitoring program and analyze system results.

It is re-emphasized that the figures given in Table XIII represent an estimate and are subject to the uncertainties described above.

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TABLE I
SHUTTLE EXHAUST PRODUCTS^a

	Mass Fra	actions	Mass in Stabilized	Total Mass Deposited to
Species	Exit Plane ^b	<u>Afterburn</u> ^C	Cloud (1000 kg) ^d	10 km (1000 kg) ^e
$A1_20_3$	3.0(-1)	1.8(-2)	44-73	150
CO	2.4(-1)	8.8(-5)	0.2-0.4	0.3
CO ₂	3.5(-2)	2.6(-2)	63-100	210
C1 ₂	1.8(-6)	1.1(-3)	2.7-4.3	10
HC1	2.1(-1)	1.2(-2)	30-50	105
H_2	2.1(-2)	4.2(-4)	1.0-1.7	3
H_2O	9.4(-2)	3.3(-2)	81-130	250
NO	1.1(-5)	5.8(-4)	1.4-2.3	7
NO ₂	- 	7.9(-6)	0.02-0.03	0.06

a From Refs. 1-3

 $^{^{\}rm b}$ A(B) denotes A x $10^{\rm B}$

Assumes 59% solid motor products, 29% solid motor products that pass through flame trench and 12% orbitor motor products. Dilution with ambient air is assumed to be 17:1. Water from entrained air not included.

Assumes 15 to 24 sec burn times. Mass is for both upper and lower portions of cloud.

e 50 sec burn time. Estimated from exit plane composition for inert species. For reacting species, final 35 sec estimated from solid and orbitor products.

TABLE II

APPROXIMATE GROUND CLOUD COMPOSITION

AT STABILIZATION^a

a .	Mass	, ,
Species	Concentration	(ppm)
Al_2O_3	60	
CO	0.3	
CO ₂	90	
C1 ₂	. 4	
HC1	41	
$_{\rm H_2}$	1	
H ₂ O	110	
$NO_{\mathbf{x}}$	2	

a Assumes overall dilution ratio of ambient air to exhaust products of 5000:1

TABLE III
WIND DIRECTION PROBABILITIES FOR CENTRAL FLORIDA

Probability of Occurrence of Various Wind Directions, % Probability of Land/Sea Westerly Southerly Easterly Wind^a Easterly January February March April May June July August September October | November December

The probability that the prevailing winds will carry the exhaust cloud inland. This probability is the sum of the easterly wind probability and that fraction of the land/sea winds that are easterly and the day for a given month. The relatively low occurrence of northerly winds is included in the land/sea, easterly and westerly figures.

TABLE IV

1975 EMISSION ESTIMATES FOR BREVARD COUNTY^a

(tons/year)

Company	Location	Part.	SO ₂	NO ₂	HC	<u>co</u>
Belcher	Port Canaveral	2	28	9	0	0
Melbourne Water	Melbourne	13	4	8	0	0
Florida P & L	Frontenac	436	10726	1136 8	564	5
General Development		8	31	17	1	1
Harris	Palm Bay	27	7	0	77	0
Macasphalt	Malabar	11	135	31	2	0
Orlando Utilities	Bellwood	2372	31992	10726	241	336
Weekly	Rockledge	24	7	0	0	0

a From National Emission Data System via Florida Dept. of Environmental Regulation, Tallahassee, FL.

TABLE V

1976 EMISSION ESTIMATES FOR LOCAL POWER PLANTS^a
(tons/year)

	<u>Particulates</u>	SO2	NO ₂
Florida Power and Light	< 1250	11898	13194
Orlando Utilities	30 0	11924	36110

From R. Allen, Florida Power and Light and W. Shoup, Orlando Utilities Commission.

TABLE VI SECONDARY NATIONAL AIR QUALITY STANDARDS FOR PARTICULATES, NO2, AND \circ 02

Species	Averaging Time	Standards, µg m ⁻³
Particulates	Annual geometric mean	60
	24 hours	150
NO ₂	Annual arithmetic mean	100
SO ₂	Annual arithmetic mean	60
	24 hours	260
	3 hours	1300

a From Ref. 15.

TABLE VII
ALLOWABLE LIMITS FOR HC1a

Exposure	Short : Public Lim		Public Emergency Limit, ppm	
Time, min	Average	<u>Peak</u>	Average	Peak
10	4	8	7	14
30	2	4	3	6
60	2	4	3	6

a From Ref. 16.

TABLE VIII INDIVIDUAL SAMPLE RESULTS FROM TI-CO AIRPORT FOR THE PERIOD 20 NOVEMBER 1976 TO 7 JANUARY 1977 a $(\mu g \ m^{-9})$

Date	<u>Particulates</u>	SO ₂	NO ₂
11/20/76	23.94	14.92	0.20
11/26/76	41.25	46.27	2.67
12/2/76	22.13	ъ	1.17
12/8/76	21.68	35.84	0.29
12/14/76	11.88		0.71
12/20/76	24.18	17.14	0.83
12/26/76	17.04	20.10	1.32
1/1/77	33.20	ъ	
1/7/77	21.78	2.26	

^a Dates represent most recent postings as of January 1977.

b Below detectable limit

TABLE IX

COMPARISON OF SHUTTLE AND LOCAL

POWER PLANT EMISSIONS^a

Species	Shuttle ^b	Power 1975	Plants 1976
HC1	1800		
Particulates	2500	2800	1550
Cl ₂	200		
$NO_{\mathbf{x}}$	100	22000	49000
CO	10	350	С
S0 ₂		43000	24000
Hydrocarbons	eris Can min	800	c

a tons per year

b assuming 40 launches per year

 $^{^{\}mathrm{c}}$ no estimate made

Off-site Analysis Methods

Method	Max. Sens. (ppm-sec)	Interferents	Meas.b	Sample Method	Status ^C
Titration	50	NaCl, SO ₂	D	bubbler	ор
Selective ion electrode	0.4	NaCl, SO ₂	D	bubbler	ор
Sampling indicator tube	10	?	D	coated tube	dev
X-ray fluorescence (Ref. 21)	≤ 25		D	filter	dev
Modified luminol chemiluminescence d	0.1		D	coated tube	dev

On-site Analysis Methods

Method	Max. Sens. (ppm-sec)	Interferents	Meas.b	Response Time	Status ^C	Cost ^e
Micro- coulometric	< 0.1	NaCl, SO ₂	С	1-2 min	op	5000
Aerosol- ionization	1 to 10	other aerosols, acidic gases	, с	5 sec	op	5000
Conductivity	0.05	NO2, NaCl	C	1-2 min	op	5000
Gas-cell correlation	5	CH4, H2O	С	few sec	dev/op	
Luminol chemi-	< 0.05	SO_2 , O_3 , NO_2	C	1-20 sec	op	

^a From Refs. 19 and 20 unless otherwise noted.

b C = concentration, D = dosage.

c op = operational, dev = under development.

d Moyer, R.H., Geomet, Inc., Pomona, CA.

e approximations, for instrument procurement only.

TABLE XI $\begin{array}{ccc} \textbf{TABLE} & \textbf{XI} \\ \textbf{AMBIENT} & \textbf{NO}_{\textbf{x}} & \textbf{MONITORING} & \textbf{TECHNIQUES}^{\textbf{a}} \\ \textbf{Maximum} \end{array}$

Sensitivity Operationb $(\mu g m^{-3})$ Cost (\$1000) Method Interferents 3 PAN, Os 0.1-0.6, (2-7)m, (sc) Colorimetric ' 10 $S0_2, 0_3$ 3-6 Amperometric sc ? 6-7 Sulfides Selective ion s¢ electrode SO₂ 3-7 30 Electrochemical sccell < 1 minimal 3**-8** c, sc Chemiluminescence 7 5 unknown Bioluminescence sc2nd Derivative UV 15 20 Absorption С Spectroscopy 20-25 1000 µg-meters С Correlation Spectroscopy

TABLE XII
PARTICULATE MONITORING TECHNIQUES

Method	Status	Output	Lab Analysis	Operation
Hi-Vol	FRM	conc.a	yes	manual
Impactor	operational	size ^a	yes	manua1
Beta Gauge	operational	conc.a	no	auto.
Piezo Electric	operational	conc.a	no	auto.
Optical Scattering	operationa l	visibility	no	auto.
Pulsed Lidar	develop	size	no	remote

Composition of collected samples is possible via suitable laboratory analysis.

a From Ref. 15

 $^{^{\}rm b}$ m = manual, sc = semicontinuous, c = continuous

TABLE XIII
ESTIMATED COSTS OF A REPRESENTATIVE AIR QUALITY MONITORING SYSTEM

				Initial Equipment Costs (\$1000)	Annual Materials Costs (\$1000)	Annual Operator Time (Man-Days)
A.	HC1	MONITORS				
	1.	EQUIPMENT				
		a. X-ray fluorometer	а	20		
		b. 50 sensors ^b		7.5	0.5	
		c. Setup ^c		10		
	2.	${ t MAINTENANCE^d}$			0.5	
	3.	OPERATIONS				
		a. Fluorometer opera	tor			40
		b. Place/collect sam	ples ^e			160
		c. Refurbish sensors	/batteries		-	40
			TOTAL	37.5	1	240
В.	ACI	D RAIN MONITORS ^f				
	1.	EQUIPMENT				
		a. 15 collectors ^g		15		
		b. pH meter		1		
		c. Setup ^h		1.5		
	2.	MAINTENANCE ¹			0.5	
	3.	operations ^j				110
			TOTAL	17.5	0.5	110
c.	NO _X	MONITORS				
	1.	EQUIPMENT				
		a. 2 monitors k		11		
		b. 2 recorders		1.5		
		c. Calibration $^{ m l}$		0.2		
	2.	MAINTENANCE/ CALIBRATION ^{TO}			0.5	
	3.	OPERATIONS ^m				_30
			TOTAL	12.7	0.5	30

TABLE XIII (continued)

			Initial Equipment Costs (\$1000)	Annual Materials Costs (\$1000)	Annual Operator Time (Man-Days)
D.	PAR	TICULATE MONITORS			
	1.	EQUIPMENT			•
		a. 2 Hi-Vol samplers n	2		•
		b. Calibration equipment	1.5		
		c. Lab equipment	3.5		
	2.	MAINTENANCE ¹		0.5	
	3.	OPERATIONS			
		a. Place/collect samples ^o			100
		b. Analysis			_50
		TOTAL	7	0.5	150
E.	SYS	TEM DIRECTOR			250
		SYSTEM TOTAL	74.7	2.5	780

NOTES

^a Costs vary widely depending on features. Manually operated units start at roughly \$12000. Automation and computer control can result in prices greater than \$50000 but a model costing about \$20000 is reportedly²¹ quite suitable for this application.

Based on a unit price of \$150. Sensor cost is less than \$5 per unit. The remainder of the cost is in the pump, batteries, flow or elapsed time indicator and assembly.

Includes estimated materials costs of \$100 for a shelter similar to those used for conventional Hi-Vol samplers, and its support, and \$100 labor costs for installation of each unit.

Upper limit. Based on assumed 10% annual pump failure rate. Includes replacement parts and labor costs for repair.

e It is estimated that approximately one day for two men, or preferably, a half day for four men will be required for both placing and retrieving the filter samples.

f Does not include water composition analysis.

Estimate based on information obtained from H. Rudolph, NASA/Kennedy Space Center.

NOTES (continued)

- $^{\rm h}$ Based on estimated cost of \$100 per unit for electric cable installation and mounting.
- Upper limit estimate for occasional motor repair or replacement. Includes parts and labor.
- Based on 1 man-day for each of the approximately 110 rainy days in the KSC area per year.
- ^k Approximate average cost of NO_X monitors with 10 μg m⁻³ sensitivity is \$5500. Comparable units are available from a number of manufacturers within the \$4700 to \$6200 range.
- 1 Includes cost for calibration gas, regulator and flow meter.
- m Estimated annual total for filter changes (\$2), drying agent replacement (\$1) and chart paper (\$2) for each of 52 weekly maintenance/calibration visits to each unit involving a total of 0.5 man-days per week and a 4-day annual allowance for repairs.
- $^{\mathrm{n}}$ Estimate based on information obtained from Ref 24.
- O Assumes 100 days of sampling (40 post launch and 60 "baseline") with 2 half-day trips per operational day for both units.

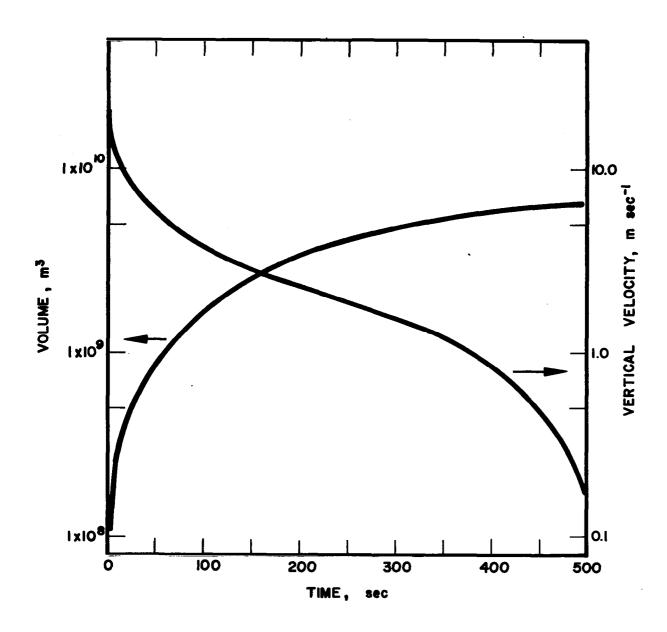


FIGURE 1 CLOUD VOLUME AND VELOCITY FOR TITAN III GROUND CLOUD PRIOR TO STABILIZATION (MAY 20, 1975 LAUNCH)

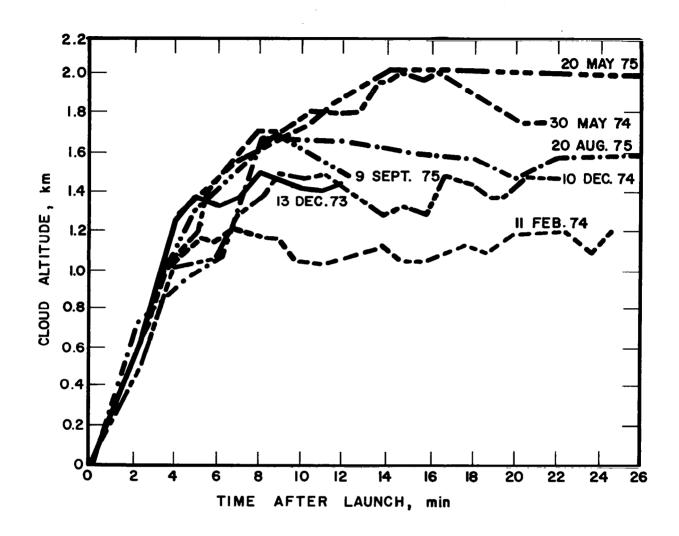


FIGURE 2 CLOUD STABILIZATION MEASUREMENTS,

DECEMBER 1973 TO SEPTEMBER 1975

(from Ref. 5)

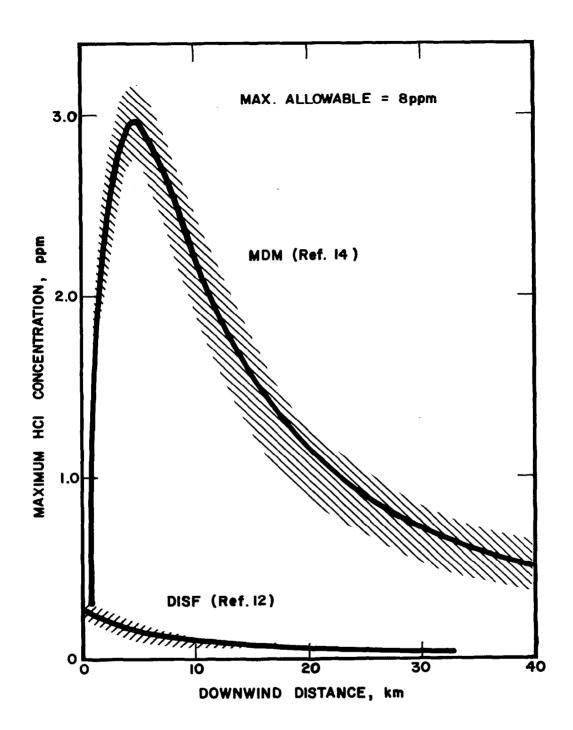


FIGURE 3 MAXIMUM DOWNWIND HC1 CONCENTRATION.

Shuttle Calculation Using Meteorological

Conditions of August 20, 1975 Titan Launch

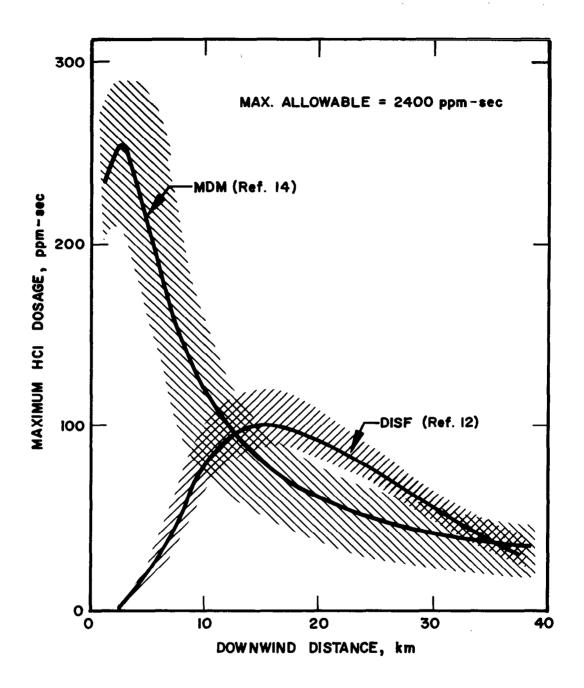


FIGURE 4 MAXIMUM DOWNWIND HC1 DOSAGE.

Shuttle Calculation Using Meteorological
Conditions of August 20, 1975 Titan Launch

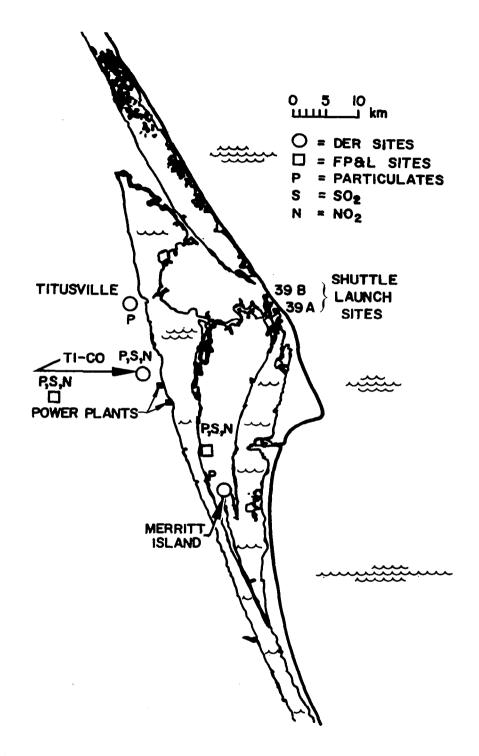


FIGURE 5 LOCATIONS OF AMBIENT AIR QUALITY MONITORING SITES IN KSC AREA

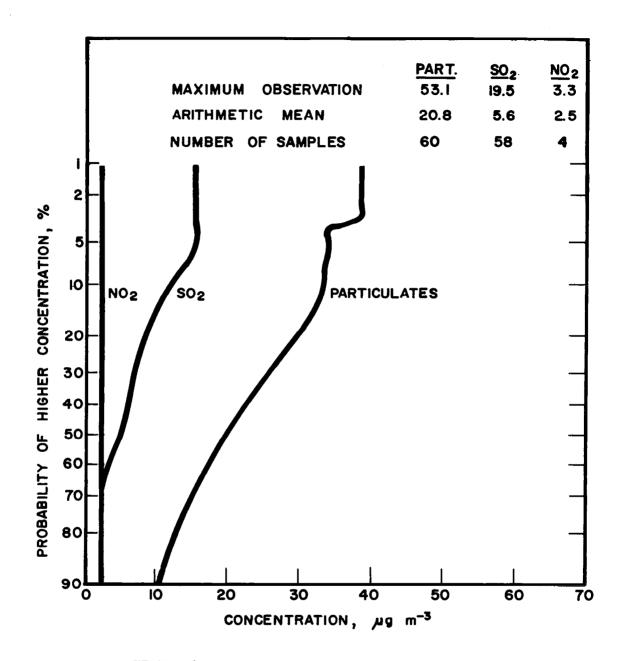


FIGURE 6 FLORIDA DER SAMPLING RESULTS AT TI-CO AIRPORT JANUARY 1975 TO DECEMBER 1975

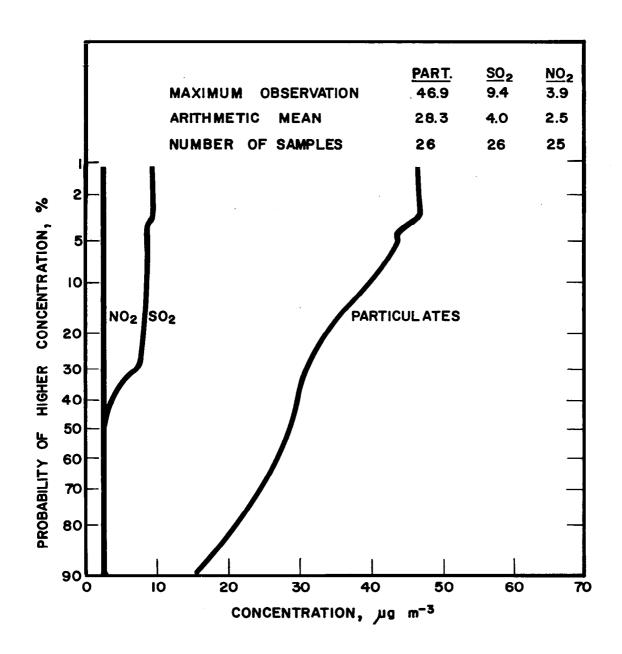


FIGURE 7 FLORIDA DER SAMPLING RESULTS AT TI-CO AIRPORT JANUARY TO JUNE 1976

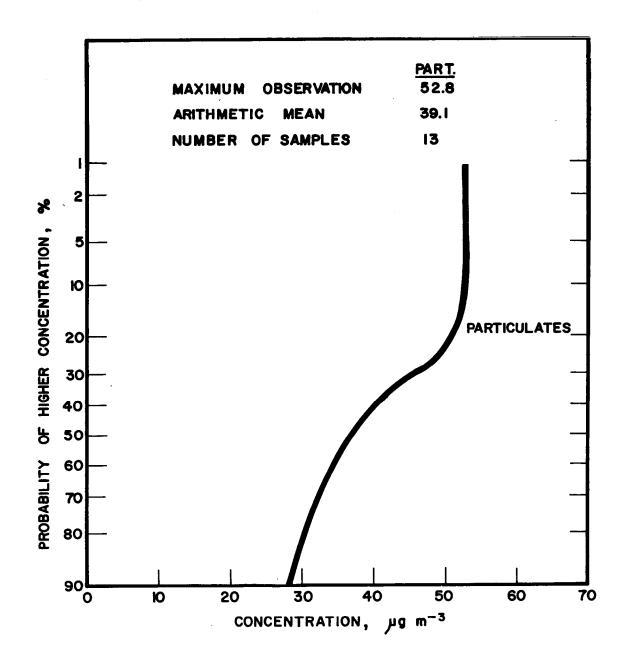


FIGURE 8 FLORIDA DER SAMPLING RESULTS AT MERRITT ISLAND APRIL 1974 TO JUNE 1976

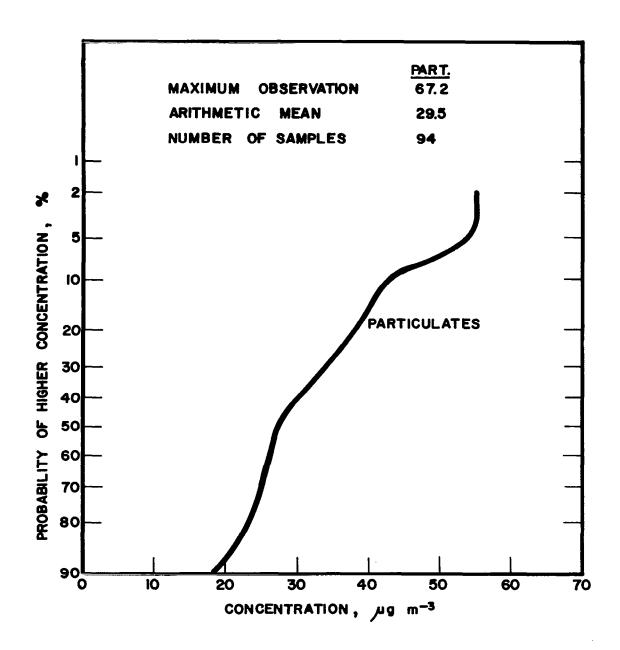


FIGURE 9 FLORIDA DER SAMPLING RESULTS AT TITUSVILLE DECEMBER 1974 TO JUNE 1976

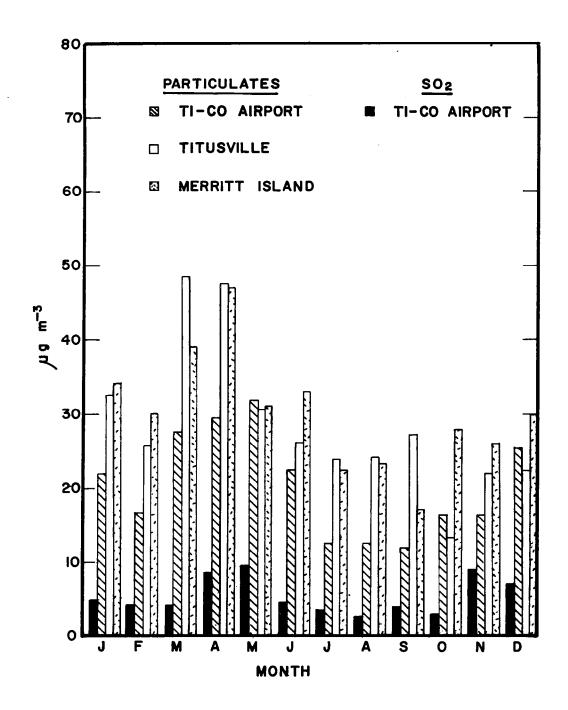


FIGURE 10 MONTHLY AVERAGES OF PARTICULATES AT MERRITT ISLAND, TI-CO AIRPORT AND TITUSVILLE; SO₂ AT TI-CO AIRPORT

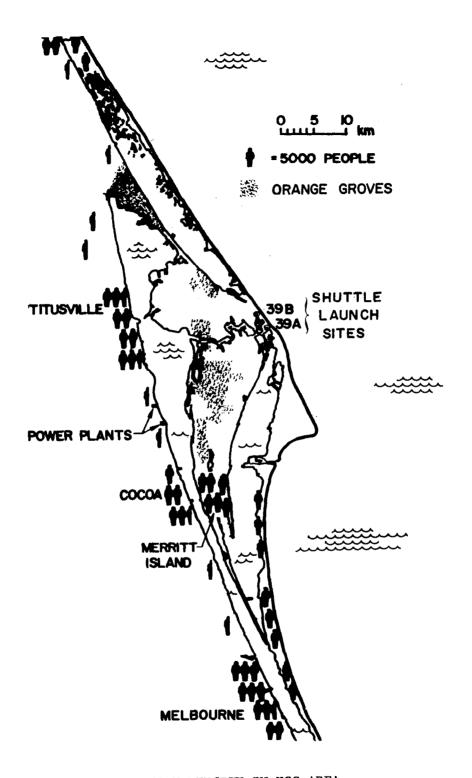


FIGURE 11 POPULATION DENSITY IN KSC AREA

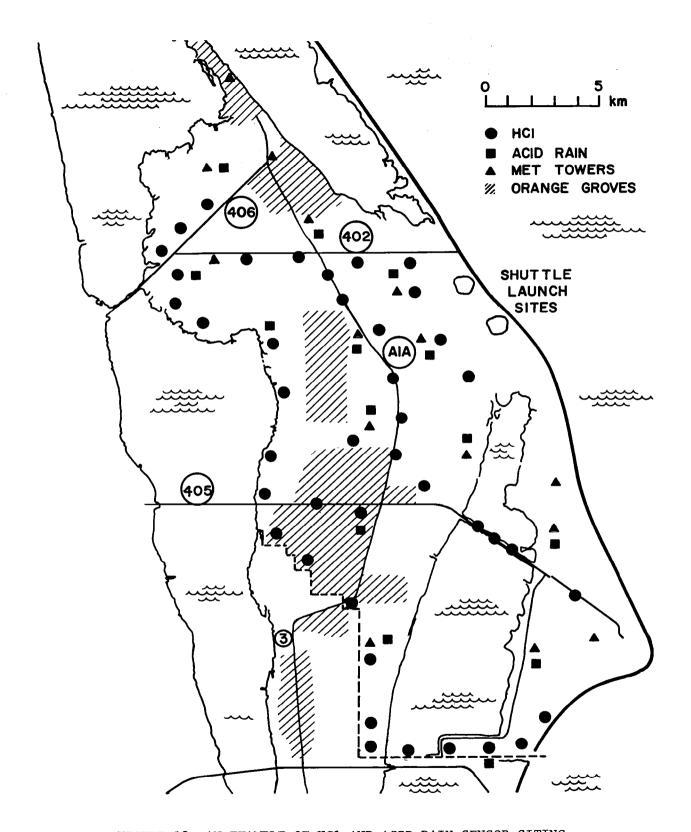


FIGURE 12 AN EXAMPLE OF HC1 AND ACID RAIN SENSOR SITING

	-	
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Langley technical monitor	: H. Scott Wagner	
Final report.		
characterize the impact o (area) of space shuttle l prevalent meteorological a cause for concern. The work of inexpensive detec rain network is also recolong-term impact involves	conditions indicates that tra	Kennedy Space Center (KSC) of ground cloud processes and ansient HCl depositions can be HCl employs an extensive net- analysis device. An acid sure of projected minimal
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HC1

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